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(54) POLYOLEFINE FILM HAVING EXCELLENT PRINTABILITY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polyolefin film which has an excellent contact with an ultra violet-setting printing ink to bring about no missing ink, an excellent coloring performance, and an excellent printability.

SOLUTION: The polyolefine film is characterized in that the outer layer which is deep up to 10 nm from the surface in at least one side of the film has following ratios in number of the constituent atoms: an atomic ratio (O/C) between oxygen and carbon which is within the range as shown by formula (1) and a ratio between an oxygen/carbon(O/C) ratio and a nitrogen/Carbon(N/C) ratio which is within the range as shown by formula (2). $0.01 \leq (O/C) \leq 0.10$ (1) $1.0 \leq (O/C)/(N/C) \leq 3.0$ (2).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] About the polyolefine film excellent in printing nature, in more detail, it excels in the wettability of ultraviolet curing mold printing ink, and adhesion, and this invention relates to the polyolefine system film excellent in printing nature suitable for printing ink and using it as a label, a seal, etc. especially.

[0002]

[Description of the Prior Art] It is pointed out that an adhesive property with printing ink or other raw materials is not [a polyolefine system film] enough in processing of printing nature, a lamination, etc. since the former to the configuration polymer is non-polar. It is said that especially the ultraviolet curing mold printing ink that became in use in the seal printing field in recent years runs short of adhesive properties with polyolefine further as compared with the printing ink of the solvent mold used for old gravure etc.

[0003] Moreover, it is regarded as questionable that printing ink is missing in the repeat activity which printing ink is missing with adhesive tape when tearing off the printing film which various problems are pointed out also in the operation, for example, stuck adhesive tape etc. on the printing side to adhesive tape, or, and strips the stuck seal in the application of a label, a seal, etc., and an improvement of the adhesion reinforcement of printing ink is desired. [an activity] [stripping from the operation, i.e., a release paper,]

[0004] To these indication, corona discharge treatment and flame treatment are performed to the front face of a polyolefine system film from the former, and surface roughening or the method of making it emasculated and raising printing ink adhesion is indicated in the approach and film front face which introduce a polar group.

[0005]

[Problem(s) to be Solved by the Invention] However, the film obtained by printing ink and the adhesion reinforcement of ultraviolet curing mold printing ink being unable to bear practical use especially, and the film obtained by carrying out corona discharge treatment of the front face carrying out flame treatment of the front face has problems which come from flame treatment equipment being an expensive rank, such as the cost high of a film product. moreover, by the approach of carrying out surface roughening of the film front face, a printing ink omission occurs by the surface projection resulting from the big and rough particle and aggregate in inorganic [for surface roughening], or an organic particle, or The printing ink omission according to a projection like the approach of carrying out surface roughening of the front face by the approach of emasculating a film, Printing ink entered to the punctured cavernous section, and in order for the lack of coloring of printing to occur or to compensate the lack of coloring, there was a trouble that the cost-problem by increasing the amount of printing ink occurred.

[0006] This invention solves the trouble which the above-mentioned conventional polyolefine system film has, is excellent in the adhesion of ultraviolet curing mold printing ink, and aims at offering the

polyolefine system film excellent in the printing nature excellent in color enhancement without a printing ink omission.

[0007]

[Means for Solving the Problem] In order to attain the above-mentioned object, the polyolefine system film excellent in the printing nature of this invention The atomic percentage of the surface section from the front face of one [at least] field of a polyolefine system film to a depth of 10nm It is characterized by being in the range of following the (1) type in the ratio (O/C) of an oxygen atomic number and a carbon atomic number, and being in the range of following the (2) type in the relation of the ratio (N/C) of the ratio (O/C) of an oxygen atomic number and a carbon atomic number, a nitrogen atomic number, and a carbon atomic number.

$0.01 \leq (O/C) \leq 0.10$ (1)

$1.0 \leq (O/C)/(N/C) \leq 3.0$ (2)

[0008] The polyolefine system film excellent in the printing nature of this invention which consists of the above-mentioned configuration excels [surface / which has the above-mentioned property] in the adhesion of ultraviolet curing mold printing ink, does not have a printing ink omission and is excellent in color enhancement.

[0009] Moreover, the total light transmission of a polyolefine system film can be 35% or less in this case.

[0010] When the total light transmission of the above-mentioned polyolefine system film is 35% or less, a film reflection factor improves by that concealment nature, and it becomes the thing excellent in the color enhancement of the printing ink printed on this film.

[0011] Moreover, the cavernous content of a polyolefine system film can be 8-30 cc / 100g in this case.

[0012] When the cavernous contents of the above-mentioned polyolefine system film are 8-30 cc / 100g, since it becomes what could develop on various labels from the descriptions, such as aesthetic property like the paper, and lightweight nature, cushioning properties, and was highly excellent also in interlaminar-peeling reinforcement, for especially the application of a pressure sensitive adhesive label etc., it is useful.

[0013] It becomes impossible that an ultraviolet curing printing ink layer is formed in the high adhesive property surface of one [at least] field of a polyolefine system film in this case further again.

[0014] The polyolefine system film with which the above-mentioned ultraviolet curing printing ink layer was formed is excellent in the adhesion of the ultraviolet curing printing ink layer formed in the high adhesive property surface, and it does not have a printing ink omission while coloring is excellent.

[0015]

[Embodiment of the Invention] Hereafter, the gestalt of the operation of a polyolefine system film excellent in the printing nature of this invention is explained.

[0016] The polio lane system film excellent in the printing nature of this invention can be obtained as follows.

[0017] In this invention, with the polyolefine system resin which forms a polyolefine system film, although polyolefines, such as polyethylene, polypropylene, and polybutene, these copolymers, or such mixture can be used, using the polyolefine system resin which uses polypropylene as a principal component is recommended from the ease of film production, and the point of stability or profitability over temperature. The polyolefine system film in this invention is a film fabricated using this polyolefine system resin, and can obtain a non-oriented film, an uniaxial stretched film, or a biaxially oriented film by the well-known approach.

[0018] A polyolefine system film still more desirable although the object of this invention is attained is a polyolefine system film containing a cavity. As an approach of forming a cavity in a polyolefine system film By blending immiscible resin, and inorganic or an organic particle with the polyolefine system resin which forms a film, and extending after film production The approach of making an interface with polyolefine system resin, immiscible resin, or a particle generating a detailed cavity, and the approach of making polyolefine system resin contain a foaming agent, making generate reactant gas with heat within an extruder, and forming air bubbles in the interior of a film are learned widely. Although the

polyolefine system film used in this invention does not ask the class of the porosi approach, the method of blending a particle, generating interfacial peeling in polyolefine system resin by drawing, and obtaining a cavity from the magnitude of the porosi, the ease of carrying out of control of an amount, etc. is recommended.

[0019] As a non-subtlety particle as a particle here, a calcium carbonate, a silicon dioxide, a barium sulfate, a magnesium oxide, an alumina, a zeolite, etc. are mentioned. Moreover, as an organic particle as a particle, a polycarbonate, polybutylene terephthalate, bridge formation polyurethane, etc. are mentioned, and if what performed various coatings to the front face of these particles further can form a cavity into a film, it can be used for arbitration.

[0020] Although the desirable magnitude of these particles changes with the thickness of a film, it is 0.5-12 micrometers about in mean particle diameter. Still more preferably, if the printing omission by foaming effectiveness or the big and rough particle is taken into consideration, it is good to use the thing of the range of 0.8-5 micrometers.

[0021] Moreover, the configuration of these particles does not ask the shape of the shape of a globular shape and a cube, cylindrical, and a cone, discoid, and an infinite form, but further, even if a particle is a porous thing, of a drawing, into a film, interfacial peeling occurs and a cavity should just be formed.

[0022] A still more desirable embodiment is that the total light transmission of a polyolefine system film is 30% or less still more preferably 35% or less. Moreover, it is desirable that it is the range whose cavernous contents of a polyolefine system film are 8-30 cc / 100g.

[0023] Moreover, although it is desirable to make total light transmission 35% or less in order to improve the beam-of-light reflection factor of a film and to improve the color enhancement of printing ink, it can attain easily by making a cavity contain in a film. In this case, the class and melt viscosity of polyolefine system resin which form a film, Although total light transmission also changes since the magnitude and the amount of a cavity change with drawing conditions, such as temperature for making a cavity discover in the loadings of the particle blended with many properties and films of a raw material, such as molecular weight, a class, a configuration, particle diameter, and a film production process, and a scale factor Only by making a film discover a cavity, when total light transmission exceeds 35%, total light transmission can also be adjusted by adding the non-subtlety particle which can give the concealment nature of a beam of light.

[0024] Although a class will not be asked if the particle used for the above-mentioned concealment of a beam of light is a thing of magnitude and description which does not generate a cavity on a film substantially by extending a film, the good titanium dioxide of a masking effect with a high refractive index is recommended. What did not ask a rutile mold and an anatase mold and performed lightfastness and various surface treatment for color tone adjustment to the front face is sufficient as the crystal structure. However, the particle diameter is number average particle diameter, and its thing with a magnitude of 0.2-0.3 micrometers is desirable at a masking effect and the point at which it does not foam substantially.

[0025] Lubricant, such as a wax and metallic soap, a plasticizer, processing aid, the well-known thermostabilizer usually added by the polyolefine film and an antioxidant, an antistatic agent, an ultraviolet ray absorbent, etc. can be suitably blended with the above-mentioned polyolefine system film in the range which does not spoil the object of this invention for the improvement in the various additives for upgrading, such as other slipping nature and antistatic nature, for example, productivity.

[0026] In order to manufacture a polyolefine system film, especially the approach of blending polyolefine system resin, inorganic or an organic particle, various additives, etc. is not limited, but after mixing to homogeneity using mixers, such as a V type blender, a screw mold blender, a drive lender, a ribbon blender, and a Henschel mixer, the approach of carrying out kneading pelletizing is common.

[0027] Thus, a film can be manufactured by the approach of illustrating below using the obtained pellet.
a: How to carry out melting extrusion of these pellets at the temperature more than the melting point of polyolefin resin, for example, the temperature of 150-300 degrees C, fabricate in the shape of a sheet, and extend subsequently with an extruder.

How to use b:2 sets of extruders, to carry out melting extrusion of the resin constituent which constitutes

the layer of other polyolefine system films from another extruder while carrying out melting extrusion of the resin constituent for forming polyolefine system film much more than one set of an extruder, pile up and carry out the laminating of them within a dice and out of a dice, and carry out a laminating subsequently.

c: How to carry out melting extrusion of remaining as it is or the polyolefine system resin layer which extends one shaft and forms a front face in the front face of one of these, or both front faces, carry out the laminating of the sheet which constitutes much more polyolefine system film which carried out extrusion molding to the shape of a sheet, and extend it subsequently beforehand.

[0028] Although the thickness of the polyolefine system film excellent in the printing nature of this invention changes with an application and operation, it is desirable that thickness is usually 10-250 micrometers.

[0029] In addition, the film production conditions of the polyolefine system film used by this invention can be extruded and extended for the temperature and the scale factor which can attain desired film physical properties and a desired cavernous content. For example, it can obtain by giving the next drawing to the sheet which solidified the film production conditions in the case of common polyolefine system resin, and not the thing that changes in any way but the resin constituent which carried out melting extrusion at temperature with an extrusion temperature of 150-300 degrees C with the 10-100-degree C cooling roller.

[0030] In a drawing process, it can extend to about 10 to 40 times preferably for an about 8 to 50-time area scale factor. Moreover, the drawing approach cannot ask 1 shaft drawing and a biaxial drawing, and, also in a biaxial drawing, can carry out by the simultaneous biaxial extending method, the serial biaxial extending method, a tubular film process, etc., but its biaxial drawing is common serially.

[0031] It extends about 3 to 8 times between the rolls which have first the peripheral-speed difference heated at 100-150 degrees C in a lengthwise direction as conditions in the case of performing a biaxial drawing serially, and subsequently to the cross direction a tenter drawing machine is used, and it extends about 4 to 10 times at the temperature of about 140-170 degrees C. After performing heat setting processing at temperature with an extent of 150-170 degrees C after an appropriate time, it is obtained by rolling round.

[0032] The polyolefine system film excellent in the printing nature of this invention The atomic percentage of the oxygen of the surface section from the front face of the field of one [at least] of these to a depth of 10nm, carbon, and nitrogen sets to the ratio (O/C) of an oxygen atomic number and a carbon atomic number. It is in the range of following the (1) type, and must have the range of following the (2) type in the relation of the ratio (N/C) of the ratio (O/C) of an oxygen atomic number and a carbon atomic number, a nitrogen atomic number, and a carbon atomic number.

$0.01 \leq (O/C) \leq 0.10$ (1)

$1.0 \leq (O/C)/(N/C) \leq 3.0$ (2)

Here, also in the flume gap in which the value of each above separates from the range of a formula (1) and (2), the adhesion of printing ink, especially ultraviolet curing mold printing ink serves as a defect.

[0033] As for the polyolefine system film which has the above-mentioned property, it is desirable to carry out corona discharge treatment or plasma treatment in the ambient atmosphere which does not have parenchyma top oxygen under existence of nitrogen gas, after biaxial stretching is carried out, and to be based on the approach of introducing the nitrogen atom of an imino mold or/and an amino mold into the surface section from a front face to a depth of 10nm. As the typical surface treatment approach, it can obtain using equipment as shown, for example in JP,5-9459,B etc. by carrying out corona discharge treatment under nitrogen-gas-atmosphere mind intrinsically. Although, as for processing conditions, various factors, such as a film rate, inter-electrode distance, roll temperature before processing, ambient temperature, and processing power, are related at this time, as for processing power, it is practical that it is the range of 5000 - 12000 J/m², for example. Moreover, there is a method of setting various gases to the plasma state and carrying out chemistry denaturation of the film front face etc.

[0034] Although the film which has such a surface characteristic has good printing nature and it can

print it with the printing ink of arbitration, it is a real example with desirable making it print and harden with an ultraviolet curing ink, and forming an ultraviolet curing printing ink layer.

[0035] The ultraviolet curing printing ink layer as used in the field of this invention means the printing layer which three-dimensions-constructed the bridge, hardened and was obtained by irradiating the ultraviolet rays of a 200-400nm wavelength region at the printing section printed with ultraviolet curing mold printing ink. Moreover, ultraviolet curing mold printing ink means the printing ink which can three-dimensions-construct a bridge, can harden by the exposure of ultraviolet rays in a short time, and can form a printing layer. There are an acrylate system, a thiol system, an epoxy system, a silicon system, etc. It consists of an unsaturated polyester system, a polyurethane system, an epoxy system, a silicon system, the reactant oligomer represented by silicon system acrylate, a photopolymerization nature monomer, a photopolymerization initiator, a pigment, polymerization inhibitor, a wax, etc. as a fundamental component.

[0036] Further, it may respond to the object, and the film of this invention may be added or coated with additives, such as an antistatic agent, a weathering agent, an antifogger, and a slipping agent. Moreover, according to the object, the film of this invention can perform lamination processing with embossing, printing, extrusion lamination processing, other resin films, paper, cloth, etc., and can also be used.

[0037]

[Example] Next, although an example explains the content of this invention, and the example of effectiveness, this invention is not limited to the following examples, unless it deviates from the summary. In addition, the measuring method of the weighted solidity in this description is as follows.

[0038] (1) It asked for total light transmission by all light transmission JIS-K -6714.

[0039] (2) Evaluate using interlaminar-peeling nature cellophane adhesive tape (Sekisui Chemical [Co., Ltd.] make: 12mm width-of-face and following adhesive tape ** and brief sketch). Die length presses down the adhesion side face of adhesive tape ** to 3cm with a rear-spring-supporter finger, and makes it paste it up on the front face of a polyolefine film firmly. Subsequently, a naked eye estimates the amount of the surface layer (B) which fixes a film edge with a finger, exfoliates at the include angle of 90 degrees C in 2cm/second in rate from an one direction, pastes up adhesive tape ** on an adhesive tape ** side, and peels from a laminated film.

Condition O in which a surface layer (B) does not shift to a :adhesive tape ** side at all : O A part of surface layer (B) exfoliates thinly in the layer thickness direction at an adhesive tape ** side. Condition ** which pasted the Scotch tape side and shifted : The whole surface of a surface layer (B) exfoliates thinly in the layer thickness direction at an adhesive tape ** side. Condition x which pasted the Scotch-tape side and shifted: The condition in which the whole surface of a surface layer (B) exfoliated thickly in the layer thickness direction, pasted the Scotch tape side, and shifted to the adhesive tape ** side
[0040] (3) Compute from a degree type to the cavernous volume which exists in cavernous content polyolefine system film 100g.

[0041]

[Formula 1]

$$\text{空洞含有量} = 100 \times \left(\frac{1}{D} - \frac{\sum M_i / \rho_i}{100} \right)$$

• 式中 M_i は原料別の混合割合(%)を示し、 ρ_i は各々の密度を表す。D は延伸フィルムの見掛け密度を表す。

[0042] (4) Use the number ratio ESCA spectrometer of atomic configurations (/ESCA by Shimadzu Corp. 850 mold), and it is incidence X-ray:Mg-K. The peak area of alpha rays (1254eV), the peak area for which it asked under X-ray output:9kVx30mA (output 270W) conditions from IS orbital spectrum of the carbon of the surface section from a film front face to a depth of 10nm, the nitrogen for which it asked similarly, and oxygen was measured.

[0043] The correction-by-sensitiveness value at this time is the value of the photoionization cross

section itself, and was made into actual measurement / correction value = detection reinforcement. moreover, a measurement environment -- degree of vacuum: -- it is about 10E5Pa, and the numeric value which **(ed) the ratio (O/C) of an oxygen atomic number and a carbon atomic number and the ratio (O/C) of an oxygen nitrogen atomic number and a carbon atomic number by the ratio (N/C) of a nitrogen atomic number and a carbon atomic number was calculated from the detection reinforcement of each of this element.

[0044] (5) On the printing ink printing ***** film, RI circuit tester (/RI-2 made from ***** Co. mold) was used, ultraviolet curing mold printing ink (the/trade name made from TOKA: best KYUA, 161 Japanese ink, T&K) was printed so that it might become amount of printing ink 2.0 g/m2, with the UV irradiation machine, the ultraviolet rays of 500 mJ/cm2 are irradiated, were stiffened, and the following color enhancement and adhesion were evaluated.

[0045] (a) Viewing estimated as follows the color enhancement of the printing section which performed the color-enhancing above-mentioned printing.

O : -- O: with sufficient coloring -- x:coloring which can be used practically satisfactory -- thin -- practically -- problematic -- [0046] (b) Evaluate using cellophane adhesive tape (Nichiban [Co., Ltd.] make: 18mm width-of-face and following adhesive tape ** and brief sketch) after putting the squares parallel slit (25 pieces) of 2mm spacing of every direction into the print which performed the printing ink adhesion above-mentioned printing. Die length makes 3cm paste up the adhesion side face of adhesive tape ** on the front face of a printing side firmly all over a presser foot by the click of a rear-spring-supporter finger. Subsequently, a naked eye estimates the amount of the printing ink layer (B) which fixes a film edge with a finger, exfoliates at the include angle of 90 degrees C in 2cm/second in rate from an one direction, pastes up adhesive tape ** on an adhesive tape ** side, and peels from a film.

O Condition O which does not have shift of printing ink in a :adhesive tape ** side : the printing ink with which the printing ink with which the printing ink which shifted to the adhesive tape ** side shifted to the four or less condition **:adhesive tape **'s side shifted to the condition x:adhesive tape ** 5-9 pieces side is ten or more conditions [0047]. With an extruder, (Example 1) As 99.97 % of the weight of polypropylene and the anti blocking agent for melt flow rate 30g / 10 minutes Melting extrusion of the mixture of 0.03 % of the weight of polymethylmethacrylate bridge formation particles of 4.0 micrometers of mean diameters (/EPO star MA 1004 by NIPPON SHOKUBAI Co., Ltd.) is carried out. With a 25-degree C cooling roller, to a lengthwise direction at the drawing temperature of 130 degrees C after cooling 4.3 times, 155 degrees C -- a longitudinal direction -- a 8.3 time drawing -- carrying out -- N2 concentration 99.999vol% -- under the ambient atmosphere, after performing corona discharge treatment by impression energy 9000 J/m2, it rolled round, and the polyolefine system film with a thickness of 60 micrometers was obtained.

[0048] (Example 1 of a comparison) In the example 1, the polyolefine system film was completely obtained by the same approach except having changed the corona-discharge-treatment ambient atmosphere into air.

[0049] (Example 2) In the example 1, the polyolefine system film was completely obtained by the same approach except having changed melting mixing resin into the mixture of 85 % of the weight of polypropylene, and 15% of titanium dioxides with a mean particle diameter of 0.21 micrometers.

[0050] (Example 3) Melting extrusion of 85 % of the weight of polypropylene, 12 % of the weight of calcium carbonates with a mean particle diameter of 0.26 micrometers, and the mixture of 3 % of the weight of titanium dioxides was carried out with one extruder (A horizon), the mixture of 0.5 % of the weight of silicon dioxides with a polypropylene 99.5 weight section and a mean particle diameter of 4.0 micrometers was further extruded from another extruder (B horizon), and the laminating was carried out within the dice, it extruded so that it might become the percentage of the ratio of B/A/B=1/8/1, and it fabricated in the shape of a sheet. Then, the polyolefine system film was obtained by the completely same approach as an example 1.

[0051] Such weighted solidity is shown in a table 1. Although the film obtained in the example 1 has the good adhesion of ultraviolet curing mold printing ink, the film of the example 1 of a comparison has

poor ultraviolet curing mold printing ink adhesion, and it does not bear it at practical use.

[0052] While especially the film of an example 2 had aesthetic property like paper about the film which was excellent in the color enhancement of ultraviolet curing mold printing ink, and was further obtained in the example 3, it was light, and it was what also fully satisfies interlaminar-peeling reinforcement further.

[0053]

[A table 1]

			実施例 1	比較例 1	実施例 2	実施例 3
フィルム構成	総厚み (μ m)			60	60	60
	基層組成	厚み (μ m)		60	60	60
		ポリプロピレン (重量%)	99.97	99.97	85	85
		ポリメチルメタアクリレート(重量%)	0.03	0.03	—	—
		炭酸カルシウム (重量%)	—	—	—	12
	表面層組成	二酸化チタン (重量%)	—	—	15	3
		厚み (μ m)		—	—	3
		ポリプロピレン (重量%)	—	—	—	99.5
		二酸化ケイ素 (重量%)	—	—	—	0.5
		コロナ放電処理雰囲気 (容量%)	空素99.999	空気	空素99.999	空素99.999
フィルム特性	放電原子 O/C		0.05	0.06	0.08	0.08
	処理面数比 (O/C)/(N/C)		1.4	4.3	2.4	2.8
	全光線透過率 (%)		93	93	14	16
	空洞含有量 (cc/100g)		0	0	0.3	2.5
	印刷インキ密着性		○	×	○	○
発色性			○	○	○	○

[0054]

[Effect of the Invention] According to the polyolefine system film excellent in the printing nature of this invention, when using it as a label and a seal especially, it is the outstanding film which is excellent in the color enhancement of printing, and adhesion with printing ink, and does not have an ink omission.

[Translation done.]

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CLAIMS**[Claim(s)]**

[Claim 1] The atomic percentage of the surface section from the front face of one [at least] field of a polyolefine system film to a depth of 10nm Are in the range of following the (1) type in the ratio (O/C) of an oxygen atomic number and a carbon atomic number, and it sets in the relation of the ratio (N/C) of the ratio (O/C) of an oxygen atomic number and a carbon atomic number, a nitrogen atomic number, and a carbon atomic number. The polyolefine system film excellent in the printing nature characterized by being in the range of following the (2) type.

0.01 <=(O/C) <=0.10 (1)

1.0 <=(O/C)/(N/C) <=3.0 (2)

[Claim 2] The polyolefine system film excellent in the printing nature according to claim 1 characterized by the total light transmission of a polyolefine system film being 35% or less.

[Claim 3] The polyolefine system film excellent in the printing nature according to claim 1 or 2 characterized by the cavernous content of a polyolefine system film being 8-30 cc / 100g.

[Claim 4] The polyolefine system film excellent in the printing nature according to claim 1, 2, or 3 characterized by coming to form an ultraviolet curing printing ink layer in the high adhesive property surface of one [at least] field of a polyolefine system film.

[Translation done.]